Hitchcock (R.) With the Author's compliments

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THE ACTION OF LIGHT ON SILVER CHLORIDE.[1]

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The plan of investigation, the first results of which I have the honor to bring before you at this time, was proposed by me in May, 1885. Since then I have mentioned the method several times in conversation, but it is only recently that I have been able to put it to a practical test.

The single set of experiments here described are only preliminary to a more thorough examination of the action of light, which, it is hoped, may be carried out in future. This includes a study of—

1. The action of light upon chemically pure haloids of silver.
2. The conditions which favor the decomposition of such compounds by light.
3. The products of the decomposition.
4. The activity of different parts of the spectrum in effecting the decomposition.

The subject is one which has been much studied, but we have scarcely more definite knowledge of the chemical effect of light upon the silver haloids now than was possessed in the time of Scheele, in 1777. I have been carefully over most of the literature of the subject, and it is quite extensive, but the results are confusing and contradictory. Even such an apparently simple question as whether there is a loss in weight when silver chloride is exposed to light, has only been satisfactorily settled by the recent work of Prof. Spencer Newberry. Yet the fact that chlorine is set free by the action of light was conclusively proved by Scheele, and that the quantity set free is not inconsiderable is evident from the strong odor observed.

I will not detain you by reviewing even the more important experiments recorded in the past, but will pass on to the considerations which led me to adopt a different method of experi-

[1] Read before the Chemical Section of the A. A. A. S., Toronto, 1889.

presented by the author.

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menting. Recognising that there must either be a loss in weight corresponding to the weight of chlorine set free, or else that the chlorine must be replaced by some other element, it seemed quite plausible that an oxychloride might be formed by the action of light, as has been suggested by different writers. If two atoms of oxygen should take the place of one atom of chlorine in some unaccountable manner, then no appreciable change in weight would result. Seebeck and Abney have observed that silver chloride is not acted upon by light except in the presence of moisture, and Hodgkinson concluded that an oxychloride was formed, from which he obtained a small quantity of oxygen by heating it in an exhausted tube. This experiment, and those of Dr. W. Schmid[1] on the decomposition of plumbic iodide by light, seemed to lend strength to a rather improbable hypothesis.

Nevertheless, the subject seemed to deserve a more critical examination, and I determined as the first step not only to weigh the chloride before and after exposure to light, but also to determine the amount of chlorine set free. If an oxychloride is formed, the weight of chlorine set free must exceed the loss in weight of the chloride.

But the discrepancies in the results of observations on the loss in weight were too great to be overlooked. Why, for example, should von Bibra find that there is no loss in weight, while Prof. Newberry found a very considerable change? I will answer this question as we go on. First, I wish to remind you of von Bibra's method of working. He filled small watch-glasses with white chloride and exposed them to sunlight under bell-jars for five weeks, the chloride being occasionally stirred to expose fresh surfaces. No loss in weight could be detected. The darkened product yielded no silver to nitric acid, but ammonia dissolved the greater part of it, leaving a residue soluble in nitric acid.

In thinking over the subject I became convinced that in all experiments up to this time the action of light upon the chloride has been only superficial. The energy required to effect the separation of the haloid must be considerable, for, as Draper showed long ago, even the thin film of a daguerreotype plate absorbed the active rays so effectually as to render a beam reflected from one sensitised surface inactive upon another. It therefore became

[1] Pogg. Ann. 127, 7 (1866), 493.

necessary to obtain the chloride in a very finely divided condition, in order to ensure the complete action of the light upon it.

To accomplish this result a number of thin slips of glass, such as are used for cover-glasses in mounting microscopical specimens, were numbered with a diamond, cleaned by boiling in nitric acid, washed, and placed in a desiccator over sulphuric acid. These were accurately weighed, and I may here state that throughout these experiments two, and usually three independent weighings, on different days, were made for each operation. These slips were placed on strips of glass lying on the bottom of a crystallising jar. A very dilute solution of silver nitrate was then precipitated with chlorhydric acid in a beaker, and while the glass slips were held in place, this milky liquid was poured over them. The jar was set aside in a dark closet until the precipitate had deposited. The supernatant liquid was very slowly drawn off with a siphon, and distilled water run in by the same means. The deposited chloride is extremely light and the slightest current in the water will wash it from the glasses. The siphon must therefore have one end drawn out to a rather small point, so that it shall act very slowly. This washing by decantation must be repeated many times on successive days, in order to allow the salts in solution to diffuse thoroughly through the water, for it is not safe to draw off the water entirely, leaving the surfaces of the slips uncovered. Finally the water was drawn off as perfectly as possible, and the jar set aside until the remaining water had evaporated and the slips were quite dry. They were then picked out with forceps and placed in a desiccator, where they were allowed to remain several days or a week. They were then weighed. All these operations were done by artificial light. Slips thus prepared have a beautifully even, translucent coating of white silver chloride. Print can be read through them with ease. The slips measured about ¾-inch in width by 1½ inches in length.

The slips were placed in a glass tube, drawn off at one end to receive a rubber connection from a set of bulbed U-tubes containing a solution of silver nitrate. The other end was closed with a tubulated rubber cork and connected with a hydrogen apparatus. The hydrogen was passed through silver nitrate before it entered this tube. The tube was long enough to take four slips. When all was ready the apparatus was set out on the top of the National Museum in bright sunlight at 11.15 A. M., August 19th,

and kept running until 4.30 P.M., when the slips were returned to the desiccator, and the tube and U-tubes washed out into a beaker. It should be stated that the U-tubes were shielded from the light during the experiment by a covering of black paper.

The silver chloride from the U-tubes was determined by collecting it in a porcelain crucible. After the slips had remained over night in the desiccator they were weighed, and the next day weighed again. The results are given in full in the following table I.

SUMMARY OF RESULTS.

I. *From Hydrogen Apparatus.*

No.	Wts. of Slips.	Slips + AgCl.	Wt. of AgCl.	Slips exposed.	Loss.
1	Not used.				
2	.49575	.51870	.02295	.51775	.00095
3	.45840	.47420[1]	.01580	...	...
4	.45563	.48350	.02787	.48225	.00125
5	.49955	.52405	.02450	.52285	.00120
6	.44163	.46575	.02412	.46460	.00115
7	.38590	Lost	...	...	...
8	.33080	.35370	.02290	...	...

The amount of chlorine set free by the action of light was found to be somewhat less than the total loss in weight of the four slips used, but allowing for experimental errors, the discrepancy is not considerable. I am confident that a closer agreement will be observed in future experiments. The results were:

Weight of crucible + AgCl,	4.0143
" " "	3.9982
" " AgCl,	0.0161
Chlorine collected,	0.0040
Total loss in weight of slips,	0.0045

Prof. Newberry dissolved a quantity of silver nitrate corresponding to 0.1 gram of chloride in water and precipitated the chloride with sodium chloride. The precipitate was exposed to direct sunlight while a current of air was passed through the liquid. The precipitate was then weighed on a Gooch filter.

[1] This slip was not more than two-thirds covered, as it was displaced in the precipitating jar and slid partly under one of the other slips.

From preliminary experiments he found that the precipitated chloride, before exposure to light, weighed .0996 to .0997 gram instead of 0.1000 gram. The metallic silver was weighed after dissolving out the chloride on the filter with ammonia. His results are thus given after exposure to sunlight:

	Weight.	Loss.	Met. Ag.	Met. Ag calc. from loss.
1	.0967	.0029	.0054	.0085
2	.0979	.0018	.0076	.0054
3	.0969	.0027	.0078	.0081
4	.0982	.0015	.0062	.0045

Placing the results of Prof. Newberry's experiments and of my own side by side, and reducing them both to represent the loss in weight of .1 gram of silver chloride, we have these figures:

		Loss.	
	Weight of AgCl.	Newberry.	Hitchcock.
1	0.1000 gram.	.003	.00418
2	0.1000	.0018	.00448
3	0.1000	.0027	.00490
4	0.1000	.0015	.00485

Two slips prepared as above, numbered 3 and 8 in table I, were exposed under a beaker-cover, without a current of gas or any attempt to collect the chlorine set free. The dry chloride taken from the desiccator was scarcely discolored in an hour in bright sunlight. A drop of distilled water on one of the slips caused immediate discoloration in the sunlight, confirming the idea that moisture is necessary for the reaction. The discoloration went on more slowly than in the hydrogen apparatus, and the exposure was continued for two days. The results show that in my experiments with the hydrogen apparatus the decomposition was not complete. The experiment should have continued over two days. It will be a matter of subsequent experiment to determine how long the action of light must continue to ensure its full effect.

The results of this last experiment are as follows:

No.	Glass.	Glass + AgCl.	Wt. of AgCl.	After Exp.	Loss.	Calc. for .1 gram.
3	.4584	.4742	.0158	.47325	.00095	.0060
8	.3308	.3537	.0229	.35230	.0014	.0062

It would appear that while the limit of the action of light may not have been reached even in the last experiments, the action

proceeds regularly and is proportionate to the duration of the exposure, when the chloride is thus finely divided.

It will be obvious, from a consideration of the figures, that the results cannot be accepted as final, for it is doubtful whether the product representing the ultimate action of light has yet been obtained. It has not been deemed profitable to speculate upon the composition of such a product at this stage of the experiments.

I would state, however, that the product of the action of light in one experiment (slip No. 3) gave up a very considerable portion of silver when heated with dilute nitric acid. This fact, so directly opposed to all previous results, conclusively shows that the action of the light in these experiments has proceeded further among the particles than in those performed in the usual manner with the chloride in mass. The presumed protective action of a large excess of unchanged chloride upon the product of the reduction is to a great extent eliminated, and we find that product to be readily soluble. The bearing of this fact upon the sub-chloride hypothesis, and also upon the researches of M. C. Lea on his photo-salts of silver, is obvious.

Perhaps more may justly be claimed for the method than for the few preliminary results. I see no reason why the method should not lead to a solution of the problem of the action of light on the haloids of silver. We may thus accurately determine:

1. The loss of weight when light has fully acted on the compound.

2. The weight of the haloid set free by that action.

From these results one can readily determine whether or not the action is merely a setting free of the haloid, or the formation of a compound of silver with some other element, as oxygen for example, at the same time. The results already obtained clearly show, to my mind, that there is no such double decomposition, but they must yet be verified. Water seems to be necessary to the reaction, but it probably does not suffer decomposition.

In conclusion, I would express my indebtedness to Prof. F. W. Clarke, Chief Chemist of the Geological Survey, for affording me the laboratory facilities for carrying on this work, and also to Dr. Carl Barus for the use of the fine Bunge balance belonging to the physical laboratory of the Survey, on which all the weighings were made.

WASHINGTON, D. C., *August* 23, 1889.